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Section 29

AUSTRALIA

corr. to EP 0 469 405

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

I/We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[54] Invention Title: AQUEOUS POLYMER DISPERSIONS

[72] Name(s) of actual inventor(s):

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of
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BASIC CONVENTION APPLICATION(S) DETAILS

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30th July 1990

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By my Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

Louis C. Gebhardt

26th July 1991

(Date)

Registered Patent Attorney

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(19) AUSTRALIAN PATENT OFFICE

(54) Title
AQUEOUS POLYMER DISPERSIONS

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(57) Claim

1. An aqueous polymer dispersion obtainable by polymerizing a monomer mixture which contains from 10 to 100 % by weight of halogenated monomers in the presence of from 0.5 to 6 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic surfactants by radical emulsion polymerization in aqueous medium, and adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to from 5 to 10 by addition of bases which are different from ammonia and from primary and secondary amines, it being possible for the bases to be added before, during and/or after the emulsion polymerization.

2. An aqueous polymer dispersion as claimed in claim 1, obtainable by polymerizing the monomer mixture in the presence of from 0.5 to 4 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic surfactants.

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COMPLETE SPECIFICATION
(ORIGINAL)

Class

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Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority

Related Art

Name of Applicant:

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Complete Specification for the invention entitled

AQUEOUS POLYMER DISPERSIONS

The following statement is a full description of this invention, including the best method of performing it known to us

Aqueous polymer dispersions

5 The present invention relates to aqueous polymer dispersions which are obtainable by polymerizing a monomer mixture which contains from 10 to 100 % by weight of halogenated monomers in the presence of from 0.5 to 6 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic surfactants by radical emulsion polymerization in aqueous medium, and adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to from 5 to 10 by addition of bases. 10 which are different from ammonia and from primary and secondary amines, it being possible for the bases to be added before, during and/or after the emulsion polymerization.

15 Aqueous polymer dispersions with halogenated monomers incorporated in the polymer have versatile uses as binders, especially where it is important to prevent fire, because films formed from them have a reduced tendency to catch fire.

20 It is known that the aqueous phase of aqueous polymer dispersions prepared without basic auxiliaries usually has a $\text{pH} < 5$, which is a disadvantage for many uses, so that the pH is generally increased by adding bases.

25 DE-A 2,246,499 discloses increasing the pH of the aqueous phase of aqueous polymer dispersions with vinyl chloride and/or vinylidene chloride incorporated in the polymer by adding basic substances such as ammonia, alkali metal hydroxide solution, amines, sulfides or 30 basic compounds of metals from group 2 of the periodic table. However, the disadvantage of these polymer dispersions is that the originally white dispersions become brown on neutralization, although, according to DE-A 2,246,499, the least discoloration occurs when ammonia is used as basic substance. The discoloration 35 described in DE-A 2,246,499 can be essentially suppressed

by addition of an epoxide.

5 It is an object of the present invention to provide aqueous polymer dispersions which have halogenated monomers incorporated in the polymer, whose pH is adjusted to from 5 to 10 by addition of bases and which, together with the films formed from them, display essentially no discoloration even without addition of an epoxide and even on prolonged storage.

10 We have found that this object is achieved by the aqueous polymer dispersions defined in the first paragraph.

15 Preferred halogenated monomers are vinyl bromide, vinyl chloride and vinylidene chloride, and of these vinyl chloride and vinylidene chloride are particularly preferred. Examples of suitable comonomers are esters of acrylic or methacrylic acid with aliphatic alcohols containing from 1 to 10 carbon atoms, preferred esters being methyl, ethyl, isopropyl, n-, iso- and tert-butyl, n-hexyl and 2-ethylhexyl esters. Further suitable
20 comonomers are carboxylic acids with α, β double bonds such as acrylic and methacrylic acid, vinyl esters of lower alkanecarboxylic acids such as vinyl acetate and vinyl propionate, nitriles of lower carboxylic acids with α, β double bonds such as acrylonitrile and methacrylonitrile, and the amides of these acids, acrylic or
25 methacrylic esters with lower polyhydric alcohols, unsaturated sulfonic and phosphonic acids, but also, for example, lower mono- or polyunsaturated hydrocarbons such as ethylene, propene and butadiene. Preferably from 20 to
30 90 % of the total weight of monomers to be polymerized comprises halogenated monomers.

35 Particularly suitable polymerization initiators are inorganic peroxides such as sodium, potassium or ammonium peroxydisulfate and hydrogen peroxide. Also suitable are azo compounds such as 2,2'-azobisisobutyronitrile and organic peroxides such as dibenzoyl peroxide, t-butyl perpivalate or hydroperoxides such as t-butyl

hydroperoxide as well as combined systems composed of at least one organic reducing agent and at least one peroxide and/or hydroperoxide, eg. t-butyl hydroperoxide and sodium hydroxymethanesulfinate, and combined systems which additionally contain a small amount of a metal compound which is soluble in the polymerization medium and whose metallic component is able to occur in several valency states, eg. ascorbic acid/iron(II) sulfate/sodium peroxydisulfate, the ascorbic acid frequently being replaced by sodium hydroxymethanesulfinate, sodium sulfite, sodium bisulfite or sodium metabisulfite.

The amount of polymerization initiator employed for the emulsion polymerization is preferably kept low and is usually from 0.05 to 1 %, preferably from 0.1 to 0.3 % of the weight of the monomers.

Preferably used as surfactants are exclusively anionic and/or non-ionic emulsifiers.

Non-ionic emulsifiers are preferably employed are ethoxylated alkanols (from 2 to 100 EO, C₈-C₃₆-alkyl), ethoxylated alcohols containing 1 to 4 olefinic double bonds (from 2 to 100 EO, C₈-C₃₆ chain), ethoxylated mono-, di- or tri-alkylphenols or -naphthols (from 2 to 100 EO, C₄-C₃₆-alkyl), ethoxylated aliphatic monocarboxylic acids (from 6 to 50 EO, C₈-C₂₄-alkyl) and ethoxylated monocarboxylic acids containing 1 to 4 olefinic double bonds (from 6 to 50 EO, C₈-C₂₄-alkyl).

Anionic emulsifiers which are advantageously employed are the alkali metal and ammonium salts of sulfated derivatives of alkanols containing from 6 to 18 carbon atoms, alcohols containing from 6 to 18 carbon atoms and 1 to 4 olefinic double bonds, ethoxylated alkanols (from 4 to 30 EO, C₁₂-C₁₆-alkyl), ethoxylated alcohols containing 1 to 4 olefinic double bonds (from 4 to 30 EO, C₁₂-C₁₈-alkyl) and of ethoxylated alkylphenols (from 4 to 30 EO, C₈-C₁₄-alkyl), the alkali metal and ammonium salts of saturated and unsaturated carboxylic acids (C₈-C₂₄- chain), the alkali metal and ammonium salts

of alkylsulfonic acids containing from 12 to 18 carbon atoms, and the corresponding salts of alkylarylsulfonic acids (C_{10} - C_{18} -alkyl) and of esters of sulfosuccinic acids with alcohols containing from 4 to 18 carbon atoms.

5 The total amount of surfactants employed is preferably from 0.5 to 4 % of the weight of the monomer mixture.

10 The emulsion polymerization is usually carried out at from 30 to 90°C. However, dispersions according to the invention which are particularly free of discoloration are obtained when the polymerization is carried out at from 30 to 70°C. The polymerization medium can be composed either of water or of mixtures of water and liquids miscible therewith, such as methanol, but water
15 is preferably used alone. The polymerization can be carried out either as a batch process or as a feed-in process, including a stepwise or gradient procedure. The feed-in process is preferred and entails part of the polymerization mixture being introduced into a vessel and
20 heated to the polymerization temperature, and then the remainder being introduced continuously, stepwise or with a superimposed concentration gradient in separate feed mixtures, one or more of which contain the monomers in pure or emulsified form. The solids content of the
25 resulting aqueous polymer dispersion is generally from 5 to 60 % by weight.

30 Particularly suitable bases for increasing the pH are metal salts of weak acids, eg. alkali metal acetates, formates or carbonates, tertiary amines such as triethylamine, but especially alkali metal and alkaline earth metal hydroxides or oxides such as KOH, NaOH and $Ca(OH)_2$, of which $Ca(OH)_2$ is particularly preferred.

35 Surprisingly, both the aqueous polymer dispersions according to the invention and films formed therefrom display essentially no discoloration even after prolonged storage.

EXAMPLES

a) Preparation of initial dispersions D1 to D8

D1: A mixture of 25 kg of water, 0.02 kg of emulsifier I, 0.03 kg of sodium peroxydisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and 0.0005 kg of iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was heated to 50°C, and 5 % of feed mixture 1 and 5 % of feed mixture 2 were added, and the mixture was maintained at 50°C for 15 min. Subsequently, while maintaining this temperature, the remaining amount of feed mixture 1 and the remaining amount of feed mixture 2 plus feed mixture 3 were added continuously and synchronously over the course of 3.5 h. This was followed by continuous introduction, likewise at 50°C, of feed mixture 4 over the course of 30 min and feed mixture 5 over the course of 1 h. After-polymerization was then carried out by addition of a mixture of 0.12 kg of a 70 % by weight aqueous/alcoholic solution of t-butyl hydroperoxide and 0.05 kg of emulsifier I in 0.35 kg of water and subsequent addition of 0.17 kg of sodium hydroxymethanesulfinate in 0.35 kg of water at room temperature.

Feed mixture 1:	55	kg of vinyl chloride
	10	kg of vinyl propionate
	35	kg of n-butyl acrylate
	1.7	kg of emulsifier II
	0.78	kg of emulsifier I and
	41	kg of water
Feed mixture 2:	0.003	kg of sodium hydroxymethanesulfinate
	0.125	kg of sodium acetate and
	14	kg of water
Feed mixture 3:	0.162	kg of sodium peroxydisulfate and
	12	kg of water
Feed mixture 4:	0.048	kg of sodium peroxydisulfate and

4 kg of water
Feed mixture 5: 0.0018 kg of sodium hydroxymethane-
sulfinate
0.0273 kg of sodium acetate and
4 kg of water

5 Emulsifier I: sodium salt of the sulfated derivative of
ethoxylated iso-octylphenol (25 EO)

Emulsifier II: ethoxylated iso-octylphenol (25 EO)

10 D2 to D4: As D1 but the emulsion polymerization was
carried out not at 50°C but at 60, 70,
and 80°C, respectively.

D5 to D8: As D1 to D4 respectively, but the amount
of sodium peroxydisulfate was increased by
50 % each time.

15 b) Addition of bases to the dispersions D1 to D8 and
examination for discoloration

20 The pH of the aqueous phase of dispersions D1 to D8
was increased to 8 by addition of ammonia, KOH, NaOH
and $\text{Ca}(\text{OH})_2$, respectively, and the discoloration was
assessed visually.

25 There was a distinct yellowing when ammonia was
used, while there was only a faint yellow tinge when
KOH and NaOH were used, and there was no discolora-
tion when $\text{Ca}(\text{OH})_2$ was used. When discoloration
occurred, the intensity increased from D1 to D8.

Films were then formed from the alkaline dispersions
and were stored in an oven at 50°C for 14 days and
again assessed visually for discoloration. The
results corresponded to those for the liquid state.

~~Wherein:~~ THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An aqueous polymer dispersion obtainable by polymerizing a monomer mixture which contains from 10 to 100 % by weight of halogenated monomers in the presence of from 0.5 to 6 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic surfactants by radical emulsion polymerization in aqueous medium, and adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to from 5 to 10 by addition of bases which are different from ammonia and from primary and secondary amines, it being possible for the bases to be added before, during and/or after the emulsion polymerization.

2. An aqueous polymer dispersion as claimed in claim 1, obtainable by polymerizing the monomer mixture in the presence of from 0.5 to 4 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic surfactants.

DATED this 26th day of July 1991.

BASF AKTIENGESELLSCHAFT

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Abstract of the Disclosure: Aqueous polymer dispersions are obtainable by polymerizing a monomer mixture which contains from 10 to 100 % by weight of halogenated monomers in the presence of from 0.5 to 6 % by weight, based on the monomer mixture, of exclusively anionic and/or non-ionic emulsifiers by radical emulsion polymerization in aqueous medium, and adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to from 5 to 10 by addition of bases which are different from ammonia and from primary and secondary amines, it being possible for the bases to be added before, during and/or after the emulsion polymerization.